

SCIENCE FOR CERAMICS PRODUCTION

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FEATURES OF HIGH-DENSITY INDUSTRIAL CERAMICS TECHNOLOGY. AGGREGATION OF PARTICLES OF THE INITIAL POWDERS

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Aggregation processes during production of oxide powders and compounds used for manufacturing functional ceramics by chemical methods were examined. It was shown that aggregation of powder particles prevents obtaining high-density ceramics. Process methods and conditions of manufacturing articles of high relative density were established.

The high excess energy of powders predetermines their dissipation due to particle aggregation and completion of their crystal structure. Different causes can keep particles in an aggregate: van der Waals forces, surface tension in the presence of a liquid phase, electrostatic forces, the adhesive effect of organic and inorganic substances, and solid-state bridges. For technology, it is essential that the excess energy of the body be reduced in this process, i.e., the driving force of sintering of powders must be decreased. In order to obtain a dense polycrystalline structure, aggregates must be destroyed, for example, by milling or ultrasound dispersion. In the previously examined methods [1], rapid substitution of water by an organic liquid, rapid conversion of water into ice, a high reaction rate in precipitation, etc., that is, conducting the process in essentially nonequilibrium conditions, are also very effective.

We note two fundamental processes during which particle aggregation is observed. They are production of intermediate, difficultly soluble compounds and their conversion into oxides by heat treatment. Aggregates of particles of the intermediate compounds and oxides are formed for different reasons, so that they naturally affect the structure of the synthesized solid phases differently. In particular, the properties of the powders of intermediate compounds are primarily a function of the method of obtaining them. The method of precipitation from solutions is most common in industry, so

that we will examine some aggregation processes as a function of the conditions. The structure and properties of sediments are a function of the precipitation rate, concentration of precipitated substances and precipitant, duration of precipitation, temperature, stirring speed during precipitation, solubility of sediment, pH of the medium, etc. [2]. The available information also indicates that they can also be a function of the conditions of the initial substances before contact and chemical reaction. More disperse particles that separate at a higher rate in comparison to those obtained from unfiltered or aged solutions are usually formed from solutions filtered through a porous glass filter or freshly prepared initial solutions. The effect of filtration is due to fractionation and distribution of nuclei — crystallization centers — into a large volume; boiling has a similar effect.

Aggregation in preparation and aging of powders of intermediate compounds determines their structure and properties. To obtain coarsely crystalline sediments, precipitation must be conducted comparatively slowly from dilute solutions of salts with dilute solutions of precipitant while stirring. This can also be done from hot solutions with a hot solution of precipitant, which will increase the solubility of small crystals. Finely crystalline or amorphous sediments are obtained in fast, essentially nonequilibrium processes from highly concentrated solutions without stirring with a high rate of decanting them. Particle aggregation takes place to some degree in both cases, but the shape, size, density, and strength of the aggregates are different [2, 3].

In obtaining coarsely crystalline sediments, not only formation of individual crystallites of regular shape but also their coalescence with the appearance of relatively large ac-

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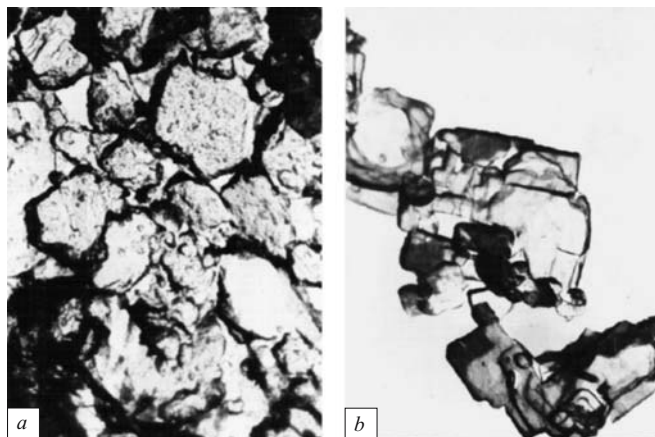


Fig. 1. Particles of scandium hydroxide powder (a) and the oxide obtained from it (b), $\times 10,000$.

cretions which are distinguished by high strength occurs in most cases. This structure is transmitted to the oxides by "heredity." An example of this phenomenon is shown in Fig. 1 for scandium hydroxide precipitated at 90°C and then annealed at 800°C : the oxide powder inherits the coarsely crystalline structure, which consists of large ($20 - 30\ \mu\text{m}$) aggregates made of well-shaped individual crystals measuring $5\ \mu\text{m}$ and less. The aggregate structure of such oxides frequently does not allow preparing densely sintered ceramics from them even when high pressing pressures are used for grinding the aggregates. Reducing the precipitation temperature decreases the size of the aggregates and significantly improves sintering of the pressed pieces. This is due to a decrease in the rate of dissolution of small crystals and the growth rate of large crystals, which on the whole decreases the size of the powder particles, degree of aggregation, and size of the aggregates. The strength of the aggregates decreases, which results in their destruction in molding the samples and improvement of subsequent sintering.

Data on sintering of scandium oxide pressings where the powders were obtained by precipitating scandium oxalate from dilute chloride solutions at $20 - 90^{\circ}\text{C}$ and sintering at 800°C are reported in Table 1 as an example.

One way of reducing the degree of aggregation of intermediate compound powders is thus to use precipitation from dilute solutions at room and even low temperature, which limits oxide crystal growth and aggregation. However, this

does not solve the problem of obtaining a highly dense ceramic, since the powders of the intermediate compounds must be fired at low temperatures, and the oxides obtained are characterized by high dispersion of the particles, while the pressings from them are sintered with high shrinkage, which is frequently unacceptable in industry. Firing at high temperatures causes the powder crystals to grow and increases the degree of aggregation of the oxides, so that additional process operations are required. Use of high pressing pressures does not totally destroy the aggregates, so that other, more effective process methods must be used.

Grinding is one method of disaggregation. For example, wet grinding of yttrium oxide powder consisting of large accretions of individual crystals in a planetary mill with yttrium oxide balls reduces the size of the aggregates from $30 - 40$ to $10 - 15\ \mu\text{m}$ after 10 min. Samples pressed at a pressure of 100 MPa at 1800°C are sintered to 94% relative density. An even greater effect is observed in grinding yttrium hydroxide before firing. Disaggregation for 5 min in a planetary mill produces an oxide (after firing at 700°C) with a maximum particle size of approximately $2\ \mu\text{m}$. Samples of this powder, pressed under 100 MPa pressure, are sintered at 1750°C to a density of 97.5% of the theoretical. The ceramic has a homogeneous structure with a crystal size of $12 - 15\ \mu\text{m}$ and zero open porosity.

Using concentrated solutions of salts in precipitation of difficultly soluble compounds is a very promising method, since finely crystalline or amorphous sediments and correspondingly, finely crystalline oxide powders, are obtained from them. The growth of primary particles is restricted or even halted. They are crystals of incomplete structure with a large number of defects. The specific surface area of such powders reaches $100\ \text{m}^2/\text{g}$, and they have high surface energy. This creates conditions for the appearance of enlarged aggregates due to confluence of the particles formed at the beginning of precipitation into blocks. However, the initial particles constituting the aggregates remain small, so that their disaggregation before firing allows obtaining highly disperse oxides.

Spraying heated ($100 - 110^{\circ}\text{C}$) concentrated solutions of salts increases the supersaturation coefficient even more, which results in small primary crystals. In addition, the reverse order of precipitation (addition of the solution to the precipitant at 20°C or cooled to low temperatures) restricts the growth of primary crystals while disaggregation of the sediment makes it possible to obtain highly disperse (with an aggregate size of less than $1\ \mu\text{m}$) oxide powders. In addition, precipitation from concentrated heated solutions increases the output of the process and decreases the volume of reagents.

In precipitation from a concentrated solution by injecting it into the precipitant in the form of a thin jet, the aggregates formed are relatively large (up to $100\ \mu\text{m}$), but consist of particles less than $1\ \mu\text{m}$ in size. Disaggregation of these hydroxides significantly affects the dispersion and structure

TABLE 1

Oxalate precipitation temperature, $^{\circ}\text{C}$	Specific surface area of oxide, m^2/g	Size of oxide aggregates, μm	Relative density, %	
			pressed pieces	ceramic
20	40.5	5	52	94
60	20.6	12	56	82
90	11.5	20	58	72

* Molding pressure of 400 MPa, vacuum annealing temperature of 1750°C .

of the oxide powders obtained, which is demonstrated below on the example of a change in the size of the yttrium scandate in grinding the powders in different process production stages [4].

Dispersion of Yttrium Scandate Powders

Powder grinding variants*	Aggregate size, μm
Without grinding.	5 – 100
Before firing	< 3
After firing	1 – 60
Before and after firing	< 1

* Wet grinding in a planetary mill for 3 min.

These data confirm the high efficacy of disaggregation of precipitated sediments before firing: the size of the aggregates decreases by 30 times. According to the results of the studies, these characteristics are similar for different oxide powders and for this reason, in our opinion, grinding of difficultly soluble compounds before they are fired is a mandatory operation that ensures the required size of aggregates of the initial oxide powder.

The structure of the sediment changes on contact with the mother liquor — it ages in time. Recrystallization and aggregation of the particles are observed [2]. Aging improves their process properties: their volume decreases, they are filtered more easily, contaminants are washed out more rapidly and completely, and the contaminants are weakly sorbed. The freshly formed sediments have both an outer and an inner surface. The aging process results in completion of the crystal lattice due to a rapid decrease in the lattice. Repeated recrystallization or the primary particles takes place, primarily due to freeing of excess surface defects and dissolution of more defective regions. Point defects located inside the crystal form associates of isolated vacancies, some near the surface of the crystals move to the interfaces where they are filled by the corresponding ions from the solution. Due to this, layers with a perfect structure appear on the surface, while associates of defects which totally or partially destroy the sediment on repeated recrystallization continue to persist inside the crystals. It was found that the ripening that takes place on aging of freshly formed finely disperse sediment causes homogenization and sharp enlargement of particles of the solid phase and also results in redistribution of an initially captured impurity between phases of the sediment – solution system [5].

Processes of ripening of the sediments in the mother liquor were investigated in production of powders of solid solutions of yttrium and europium oxalates used in fabrication of an optically transparent luminescent ceramic. They were precipitated (20°C) with continuous stirring and slow addition of a nitric acid solution of yttrium and europium salts to a solution of oxalic acid. Studies of the microstructure showed that confluence of particles 1 – 2 μm in size with formation of aggregates up to 45 μm in size (Fig. 2a) is ini-

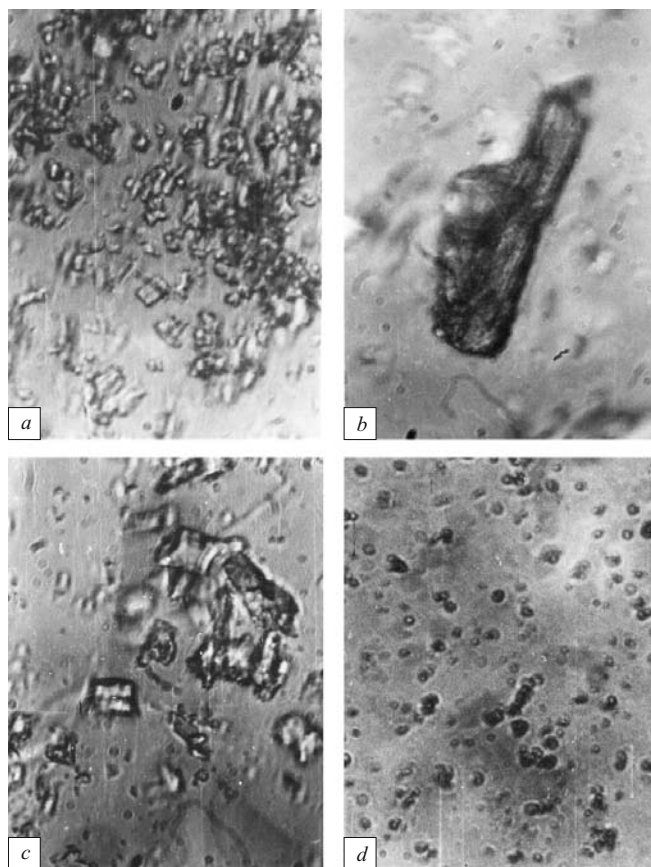


Fig. 2. Mixed yttrium and europium oxalate powders coprecipitated at room temperature ($\times 350$): a) after precipitation; b) after holding in mother liquor for 144 h; c) after firing; d) after firing of ground oxalates.

tially observed during precipitation. Increasing the aging time to 144 h causes improvement of the crystals, they acquire the prismatic shape characteristic of yttrium oxalate, and grow significantly to 15 – 20 μm (Fig. 2b). These aging conditions cause dissolution of the small particles constituting the aggregates, decomposition of the aggregates, and formation of large prismatic crystals. In firing of coarsely crystalline powders, the overall character of the structure is preserved. On conversion into oxide, they crack, probably due to the anisotropy of the stresses that arise, but the skeleton remains (Fig. 2c). Grinding with formation of round particles less than 3 μm in size and not disaggregation is observed when oxalates are ground. After firing, sufficiently finely disperse, almost unaggregated oxide particles less than 3 μm in size are obtained (Fig. 2d). After sintering, the samples of these powders have an apparent density of up to 5.07 g/cm³ in comparison with a density of 4.94 g/cm³ when unground powders are used.

In precipitation from concentrated heated solutions, aging of the sediments in the mother liquor is not necessary in most cases, since their process characteristics, the filterability in particular, are good due to the low hydration and

crystalliform character, while the defectiveness of the structure of the particles persists and is transmitted to the oxides on firing [6].

The method of heterophase reaction of solid soluble salts with a solution of an acid or a base can also be successfully used for obtaining powders of intermediate compounds in synthesis of oxides. For example, in all cases of obtaining hydroxides from the soluble salts of different elements by reaction with an ammonia solution, the shape of the particles formed is the pseudomorphosis of the initial salts. This is due to the mechanism of the reaction, where the structure of the compounds formed is given by the surface structure of the initial solid product: a new compound is formed on it, as on a matrix, and its composition is determined by the nature of the initial solid substance and the sorbed ion. This event is called destructive epitaxial growth. The elements of the structure of the hydroxides in firing are naturally inherited by the oxides [7].

The phenomenon of inheritance of the structure was investigated on the example of obtaining scandium hydroxide by reaction of scandium sulfate crystal hydrate with an ammonia solution. The powder consisted of large anisotropic crystals from 7×20 to 30×150 μm in size that almost totally replicated the shape and size of the initial sulfate particles. The scandium oxide formed on subsequent firing was characterized by a high content of large aggregates with a maximum size of 100 – 120 μm composed of particles up to 5 μm in size. Grinding of the initial salt reduced the maximum hydroxide aggregate size to 70 – 80 μm and the constituent particles were up to 3 μm in size. The oxide obtained by firing at 900°C was a poorly aggregated powder consisting of particles less than 2 μm in size and individual aggregates up to 20 – 30 μm in size. The pressings prepared from oxide powders obtained from unground and ground initial sulfate had a density of 90 and 99.5% of the theoretical density after firing.

As a consequence, the structure of the oxides can be regulated after the heterophase reaction by changing the dispersion of the initial solid salts or intermediate compounds. However, it is not always technologically convenient, or is even inexpedient and ineffective, to grind the salts. For this reason, and in the given case, disaggregation of the hydroxide can be successfully used in this case, too, and this makes it possible to obtain almost unaggregated oxide powders and to use them directly for fabricating articles, as demonstrated for yttrium-aluminum garnet. Disaggregation of hydroxides must be conducted in organic liquids alone to avoid conversion of the hydroxides into gels [6].

In many cases, primarily to obtain individual oxide powders with high dispersion and activity in sintering, the salts of different acids are used, heated at temperatures slightly higher than the crystallization temperature of the target product. In these conditions, particles with high lattice defectiveness are formed, as indicated by blurring of the x-ray peaks, low pycnometric density, and low refractive index.

All of this causes active sintering of pressings, but the oxides obtained are also subject to aggregation. The degree of aggregation, structure, and properties of the aggregates are a function of the nature of the salt and the firing temperature. For example, carbonate oxides are always distinguished by high dispersion and the absence of aggregates larger than 2 μm . Oxides from salts containing Cl^- , SO_3^- , and NO_3^- anions aggregate significantly, probably due to the fact that the surface of the particles is etched, which causes mass transfer by surface diffusion at relatively low temperatures. Increasing the heating rate at relative low decomposition temperatures always increases the dispersion of the powder obtained and decreases the size of its aggregates: in rapid realization of the process and the appearance of important stresses, intensive decomposition of the particles takes place and they cannot be joined again in a short time. These powders sinter well, but exhibit very high shrinkage. The strength of the oxide aggregates is low in most cases, and increasing the pressing pressure destroys them, which produces sufficiently satisfactory sintering at ordinary firing temperatures (1700 – 1750°C).

The nature of the initial salt and its anion part significantly affects the structure of the particles and thus their sintering. MgO powder obtained from magnesium chloride is characterized by relatively strong aggregation at 1000°C and low specific surface area, and the particles in the aggregates have a regular shape. Pressings of such material are poorly condensed and strengthened. Elevated strengthening with low shrinkage is observed in pressings at the temperature of 1350°C. This behavior indicates sufficiently high dispersion of the aggregates and defectiveness of the crystal lattice of the particles.

Yttrium oxide powder obtained from yttrium carbonate is characterized by high dispersion, the absence of aggregates larger than 2 μm , and high specific surface area. As a result of such a structure, the pressings are sintered at 1500°C to a density of approximately 95% of the theoretical density, attaining a bending strength of 100 MPa; however, the shrinkage remains high — greater than 20%.

Dry grinding in a planetary mill with a ratio of balls and material of 5 : 1 to 4 : 1 is one way of significantly improving the process characteristics of oxide powders consisting of small particles (1 – 2 μm) joined in large and strong aggregates. Intensive destruction of primary aggregates is initially observed, followed by formation of new aggregates because of compacting of particles on the walls of the drum due to a mechanical effect. Such treatment for several minutes significantly increases the bulk density of the powder and the density in pressing and improves sintering.

A number of other methods is also currently used for obtaining oxide powders and compounds: cryochemical, plasma chemical, electrochemical, sol-gel process, etc. Each one has its own features due to the specific conditions of implementation which are reflected in the structure and properties of the particles obtained. These methods require special

equipment, are somewhat laborious, their productivity is comparatively low, and most important, they have almost no important advantages in comparison to the chemical precipitation method. This method is considered as the simplest, least expensive, and most promising method in certain conditions (spraying solutions) for obtaining highly disperse oxide powders and compounds that allow solving problems in creating ceramics with a given structure and properties.

Particle aggregation is thus always observed in production of highly disperse oxide powders by chemical methods. This is especially manifested in coprecipitation of intermediate compounds from hot dilute solutions, in aging of sediment in the mother liquor, and in heterophase synthesis of such compounds from coarsely disperse salts. Significantly aggregated oxide powders are obtained after firing of aggregated intermediate compounds and their salts.

The most effective method of disaggregating these powders is wet and dry grinding of the intermediate compounds in a planetary or ball (vibro) mill.

Experience in many studies of the effect of the structure of powders allows formulating the requirements for the initial particles for obtaining high-density industrial ceramics: aggregate size of the order of a micrometer and less;

shape close to spherical;
uniform distribution of components.

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